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Microfluidic Solvent Extraction: Screen Contactors and Graphene Membranes

By Quinn McCulloch and Enkeleda Dervishi, Ph.D.

05/09/2018

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Outline

Screen contactor

- Published approaches to microfluidic LLE
- Brief history of our devices
- Screen contactor architecture
- Experiments
- Scaling
- Benefits of technology
- Future directions

Graphene Membrane contactor

- Graphene background
- Synthesis
- Experiments
- Scaling
- Benefits of technology
- Future directions
- Questions

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Screen Contactor

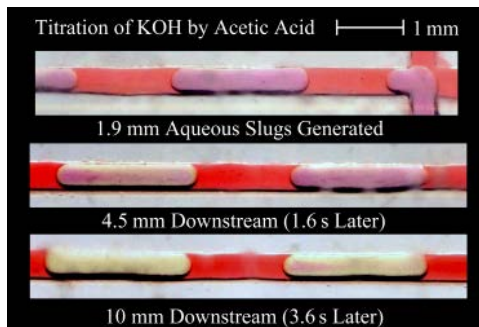
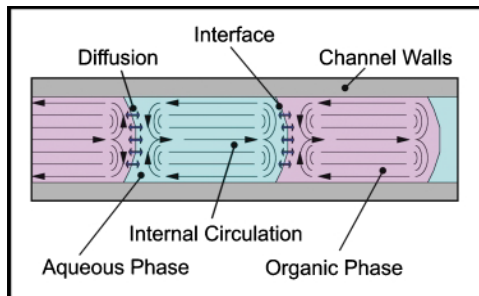
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Focus literature:

The intensification of rapid reactions in multiphase systems using slug flow in capillaries

Burns, J.R., Ramshaw, C. *Lab on a Chip*, 2001

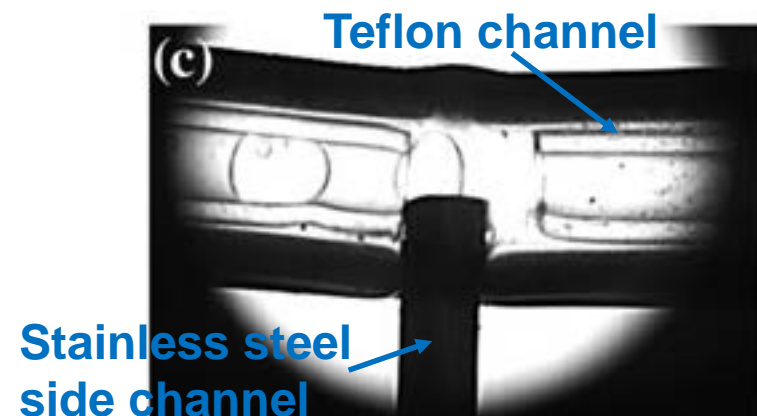
- Organic: kerosene + acetic acid
- Aqueous: KOH or NaOH
- Monitor pH change in H₂O in water
- Time-of-flight estimation of mass transfer
- No phase separation**



Studies of Intensified Small-scale Processes for Liquid-Liquid Separations in Spent Nuclear Fuel Reprocessing

Tsaoulidis, D.A. *Springer Theses*, DOI 10.1007/978-3-319-22587-6_3

- Organic: Ionic liquid + Tributyl phosphate
- Aqueous: HNO₃ + DUO₂
- Fluorescently dyed polystyrene micro beads
- Particle image velocimetry (PIV): turbulence
- UV-VIS spectroscopy: mass transfer
- Moderate phase separation using wetted materials: PTFE and stainless steel**



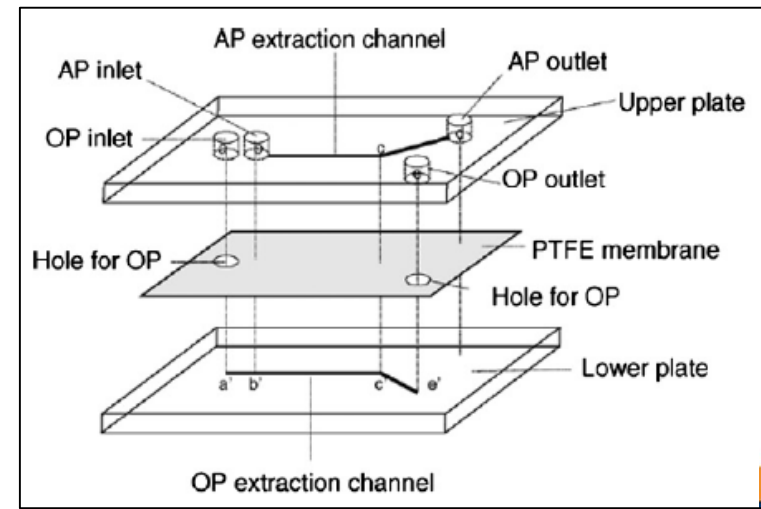
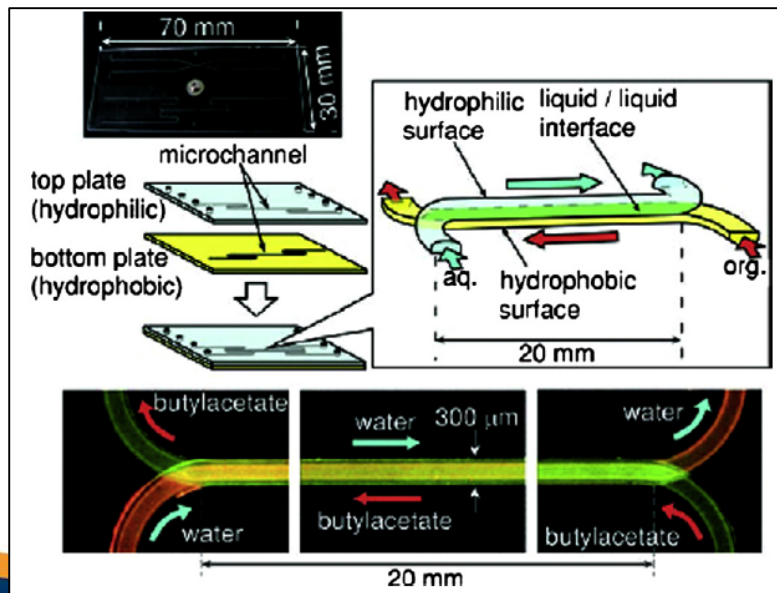
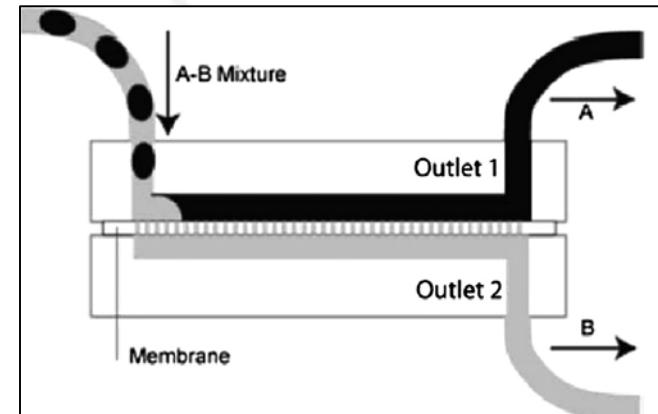
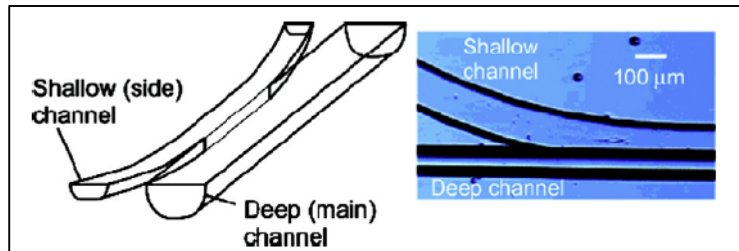
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Phase separation is required for subsequent processing

There are a variety of phase separation methods that have been attempted...

Micro-separation of fluid systems: a state-of-the-art review

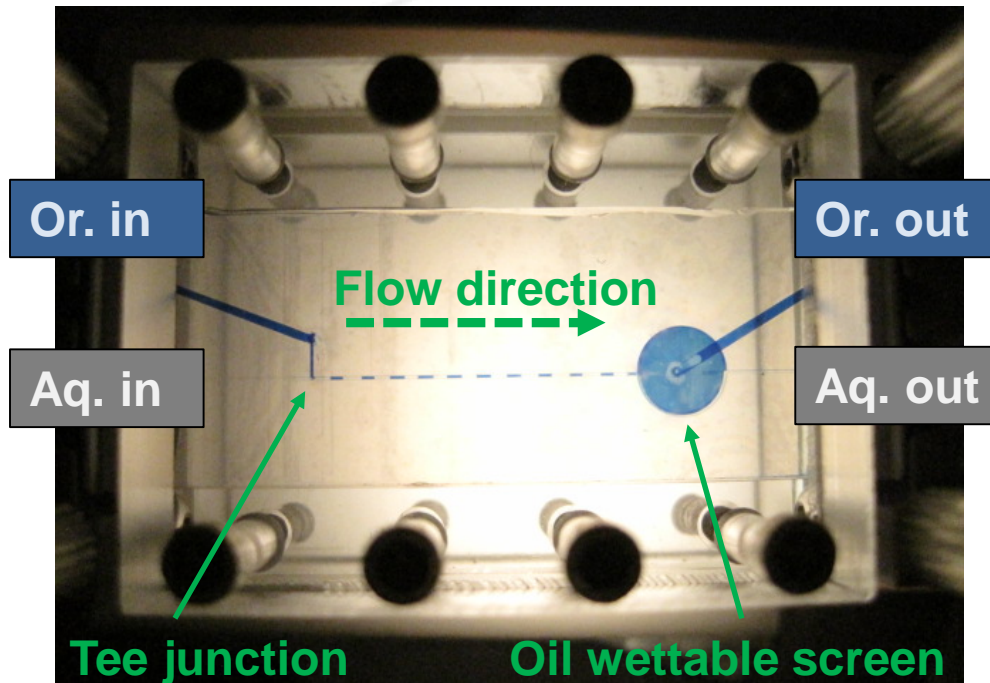
Kenig, E.Y. *Separation and Purification Technology*, 2013



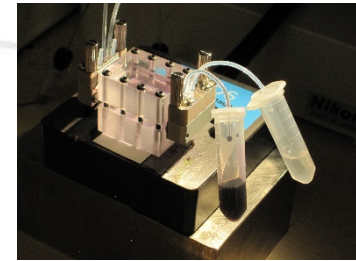
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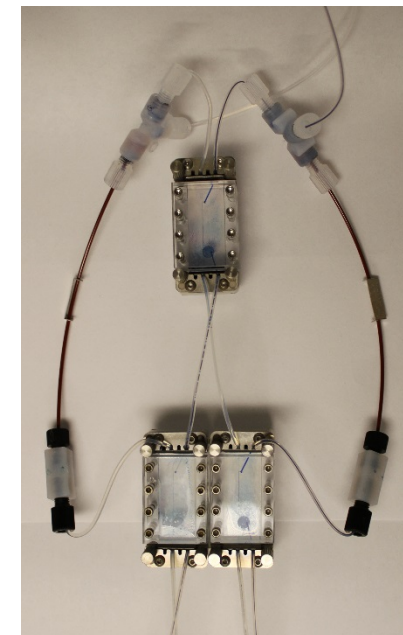
Early LANL slug flow architecture



Close-up view of a single LANL slug flow contactor possessing a $100\ \mu\text{m} \times 100\ \mu\text{m}$ channel. The chip material is quartz, which is water wettable due to its high surface energy. The circular feature is a polyether ether ketone (PEEK) screen, which is oil wettable due to its low surface energy. This pair of wettable surfaces is responsible for good phase separation.



30 hr demonstration of single stage phase separation.



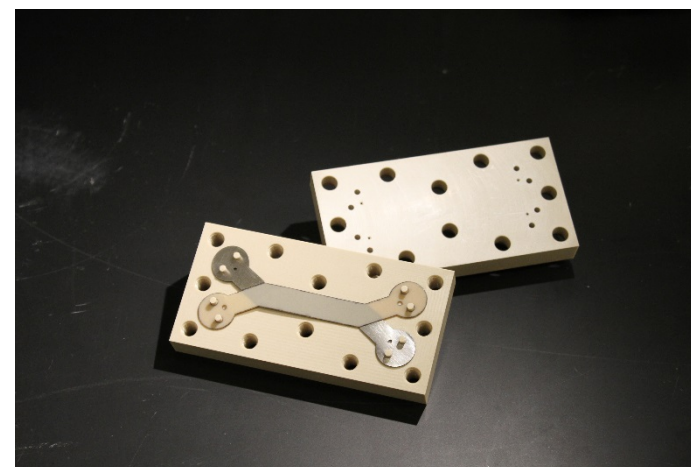
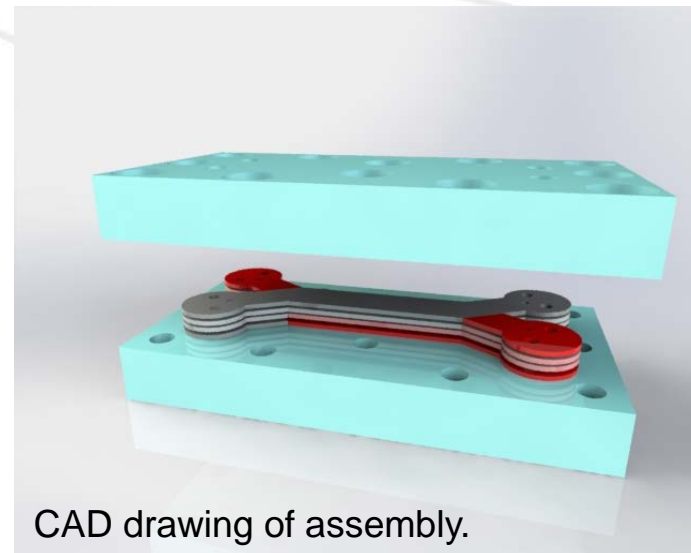
Three single LANL contactors assembled into a cascade.

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Screen Contactors

U.S. Patent Application No.
62/483,107

- Use of porous materials (mesh screens) as wettable surfaces to define biphasic liquid paths in microfluidic systems
- Screen meshes provide high surface to volume ratios necessary for liquid-to-surface adhesion and low pressure drops.

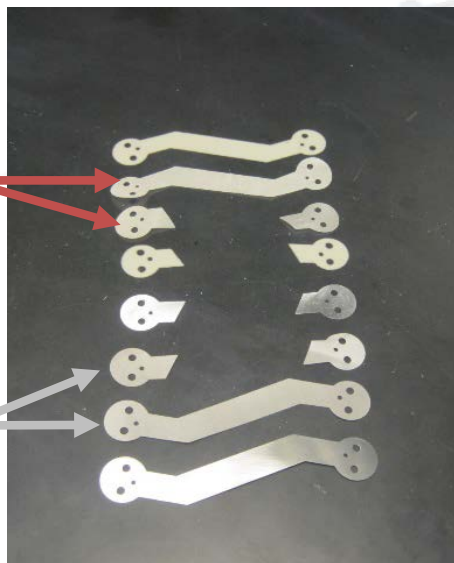


Open contactor housing.

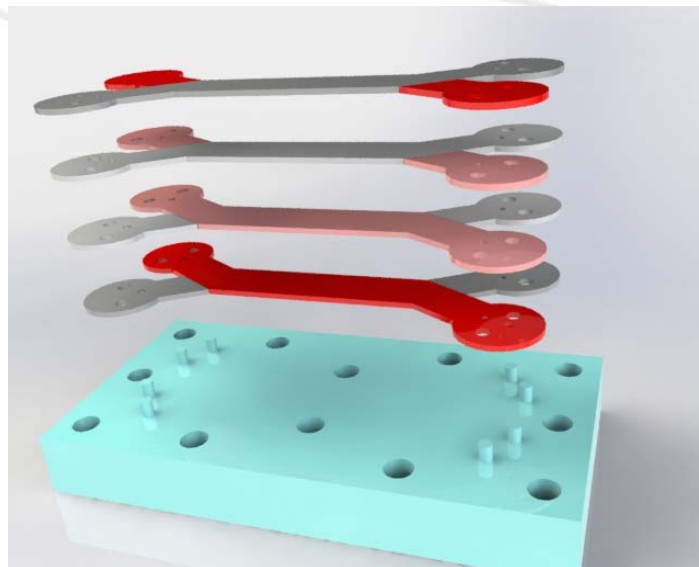
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Screen 1
(PEEK)

Screen 2
(SS)

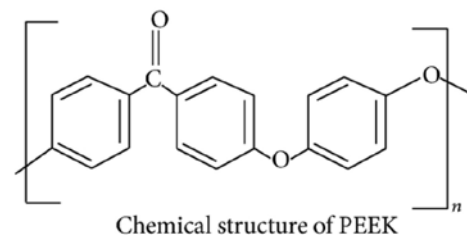


Layers used inside housing.



CAD drawing of layers, exploded view.

- Screen 1: Polyether ether ketone (PEEK) = oil wettable (non-polar surface free energy).
- Screen 2: Flame-treated stainless steel = water wettable (polar & dispersive SFE).
- Screens are 71 microns thick, which maintains micrometer length scales



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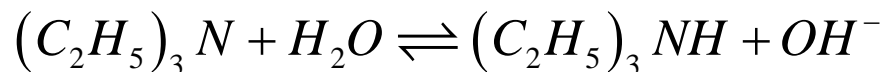
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Chemical system for flow testing: water/TEA/n-Decane

Mass Transfer Model of Triethylamine across the n-Decane/Water Interface Derived from Dynamic Interfacial Tension Experiments

Michael Fricke and Kai Sundmacher. *Langmuir* **2012**, 28, 6803-6815

- Simple base dissociation of trimethylamine (TEA)



- Well understood chemical system
- Quantifiable with a pH meter
- Doesn't degrade the stainless surfaces

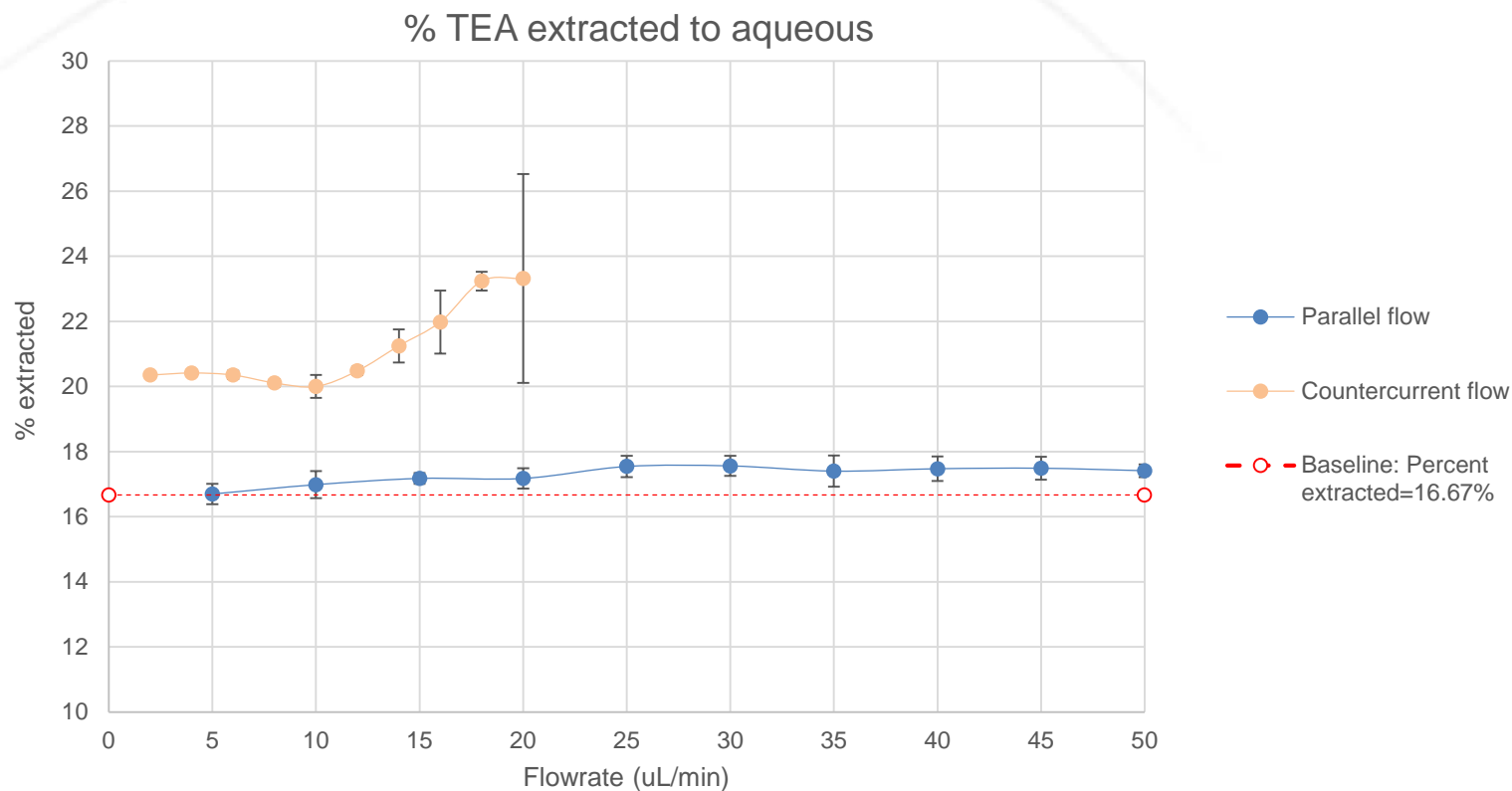
Our experiment:

1. 0.36 M TEA is loaded into n-decane
2. Solution is contacted (parallel or countercurrent) with H₂O in our cell
3. pH of the aqueous phase measured

Note: Batch equilibrium yields ~16.7% extraction into the aqueous phase.

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Triethylamine extraction results



- Starting point was 0.36 M TEA in n-decane
- Data is from single layer device

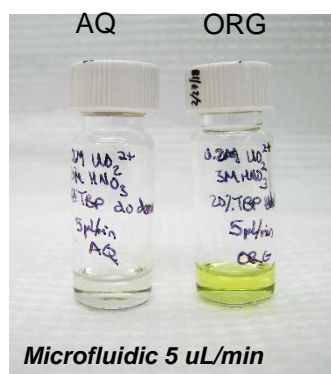
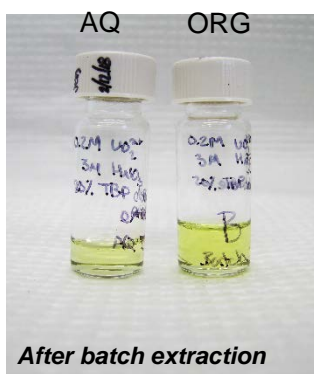
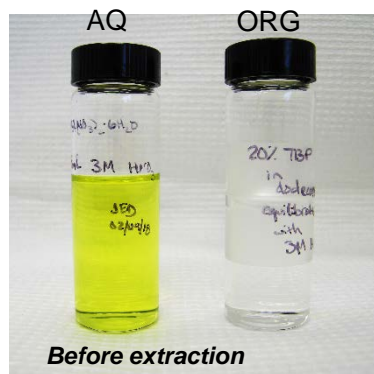
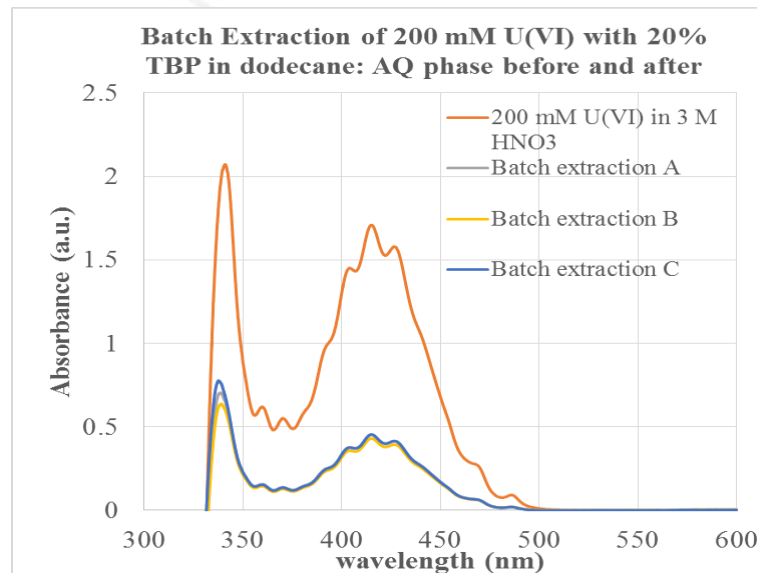
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U(VI) Extraction

Equilibrium Batch Extraction study: 1 mL of each Aq. and Or. phase contacted for 2 minutes (vortex) and then centrifuged and phases separated for storage. Triplicate samples.

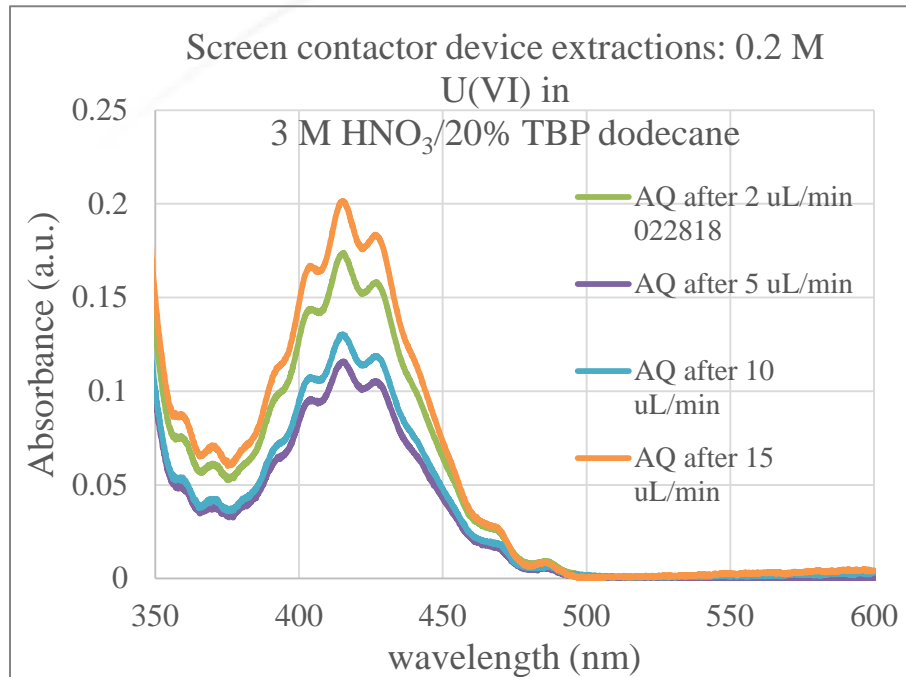
- AQ: ~ 200 mM U(VI) in 3 M HNO₃
- ORG: 20% TBP in dodecane (pre-equilibrated with 3 M HNO₃)
- The AQ was analyzed by UV-Vis spectroscopy before and after the batch extractions.
- ~75% extracted in batch studies



AVG K_d	2.83
ST DEV	0.12
ST Error	0.07
% RSD	4.31

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Microfluidic Extraction Results



UV-Vis Extraction data from 02/28/18

Flow rate ($\mu\text{L}/\text{min}$)	Absorbance (415.2 nm)	% extracted to ORG	K_d
2	0.17	91	10.1
5	0.12	94	15.6
10	0.13	93	13.8
15	0.20	90	8.6
2 (2/15/2018)	0.58	70	2.3

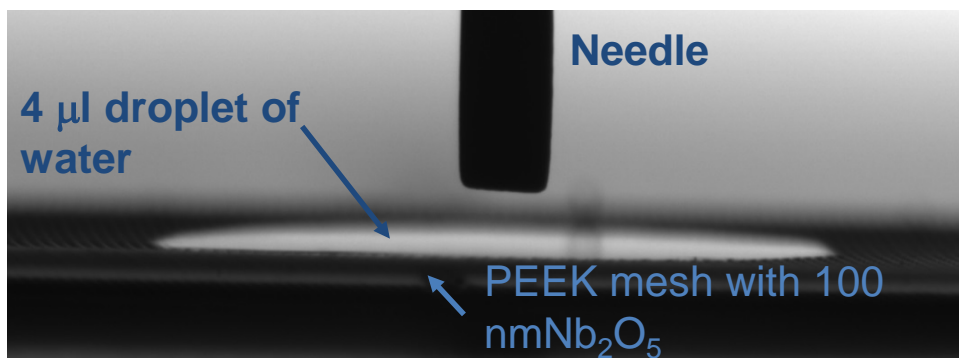
- The U(VI) extracts to the ORG phase (less in the AQ after extraction) with increased extraction as the flow rate is decreased, however maximum extraction occurred at 5 $\mu\text{L}/\text{min}$.

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Surface science: alternatives to Stainless steel and PEEK

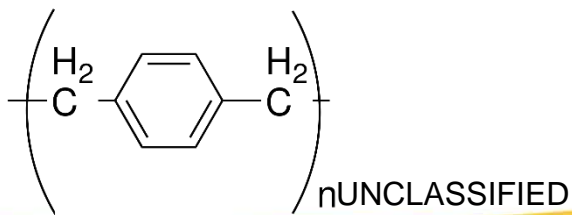
- Stainless steel corrodes in HCl and chloride-based salt solutions.
- PEEK possesses a slight polar surface free energy (SFE)
→ Fowkes Theory: Polar/Dispersive model for SFE measurements

Nb₂O₅-coated PEEK meshes and films: large SFE, water wettable and chemically resistant

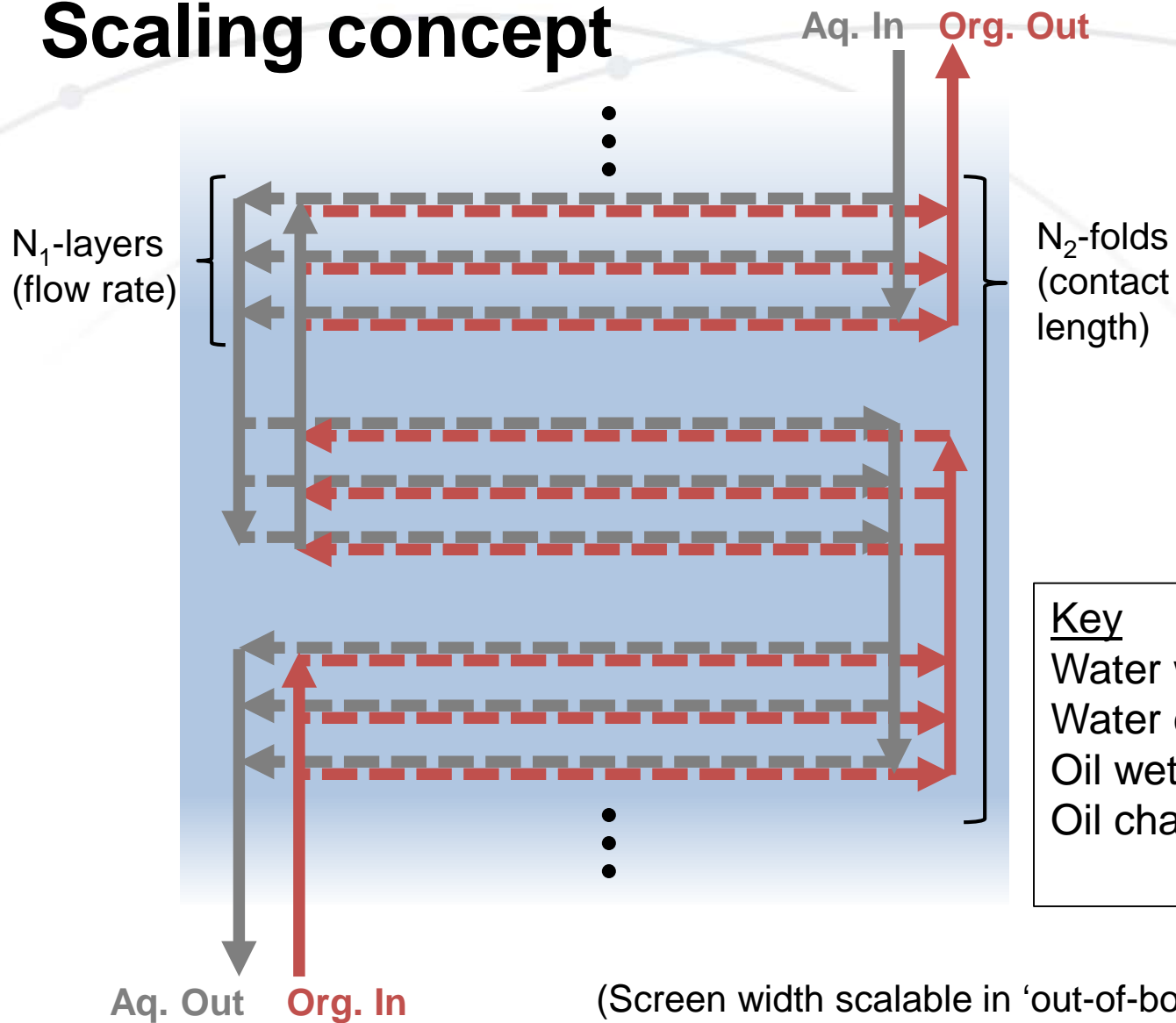


Preliminary Nb₂O₅ on stainless contact angle (receding) measurement taken using KRUSS DSA25 drop shape analysis instrument. The small (~0°) contact angle indicates excellent water adhesion.

CVD deposited Parylene-N on PEEK meshes and films: zero polar SFE, oil wettable and chemically resistant



Scaling concept



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Scaling estimate

	Current device	Scaled device
Size (inches)	2 x 4 x 1	15 x 15 x 15
Fluid contact length (m)	0.045	10
Diffusion length (microns)	71	71
Flow rate (ml/min)	0.01	1
		4 layers (250 mm x 250 mm area) interleaved, with 40 folds.
# mesh layers	1	160 total layers.
Cost: material + fabrication	<\$1000	<\$50,000



About the size of a microwave oven.

Scaling cost is primarily dependent on the cost of PEEK fabric and PEEK film; ~ \$125/sqft and \$12/sqft, respectively.

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Benefits of technology

- **No moving parts**
- Machine shop fabrication
- Microscale diffusion lengths
- Scalable in three dimensions to achieve large flow rates and path lengths
- **Minimal pumping requirements**
- Parallel and countercurrent (flow) demonstrated
- Forward \leftrightarrow reverse flow directions demonstrated (i.e. direction can be switched)

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Future work

- Surface material optimization chemistry of interest
- Increase surface area of meshes
 - currently $\sim 0.107 \text{ m}^2/\text{g}$ (BET using Kr), so there is tremendous potential here
- Thermodynamic exploration
 - Screen contactors provide a unique, membrane-free tool for studying thermodynamics
 - Screen contactors in countercurrent configuration possess unique pressure distributions
- Explore intermittent flow scheme
- Run alternative chemical systems

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Screen Contactor References

Background

- 1) Burns, J.R., Ramshaw, C. The intensification of rapid reactions in multiphase systems using slug flow in capillaries. *Lab on a Chip*, (2001), 1, 10–15
- 2) Tsaoulidis, D.A. Studies of Intensified Small-scale Processes for Liquid–Liquid Separations in Spent Nuclear Fuel Reprocessing. *Springer Theses*, DOI 10.1007/978-3-319-22587-6_3
- 3) Kenig, E. Y., Su, Y., Lautenschleger, A., Chasanis, P., Grünewald, G. Micro-separation of fluid systems: a state-of-the-art review. *Separation and Purification Technology* 120 (2013) 245–264
- 4) Fricke, M., Sundmacher, K. Mass Transfer Model of Triethylamine across the n-Decane/Water Interface Derived from Dynamic Interfacial Tension Experiments. *Langmuir* (2012), 28, 6803-6815

Patent

McCulloch, Q. Yarbrow S.L., Chamberlin, R.M., Guengerich, Q.J. Microfluidic Liquid-Liquid Contactor Based on Wettable Screens, Application No. 62/483,107 (2017).

Posters

- 1) Litchfield, S., McCulloch Q. Reliable Methods for Measuring Multiphase Contact Angles. *LANL Student Symposium*, 2017.
- 2) Guengrich, Q., McCulloch Q. Quantifying Carryover and Flow Rate in Biphasic Microfluidic Streams. *LANL Student Symposium*, 2017.

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Graphene Membrane Contactor

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Objective

Integration of graphene-based membrane systems in microfluidic devices

Development of graphene sheets (ultra thin and impermeable) as tunable and selective membrane systems for ion transport studies

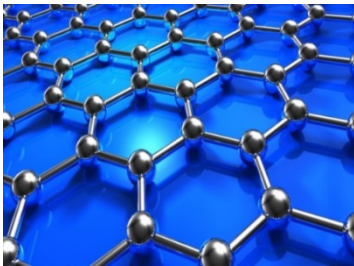
- Characterize the mechanical and chemical properties of graphene-based membranes during the reactions.
- Study the role of graphene and functionalized graphene on the reaction rate and the liquid-liquid interface phenomenon.
- Develop multifunctional graphene-based membranes for various chemical systems.

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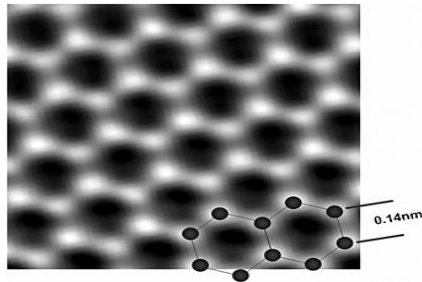
Graphene

- 2D atomic thick structure formed from hexagons of carbon atoms bound together by sp^2 hybrid bonds
- Possesses exceptional mechanical, electrical, optical and thermal properties
- An exciting material for a wide range of applications

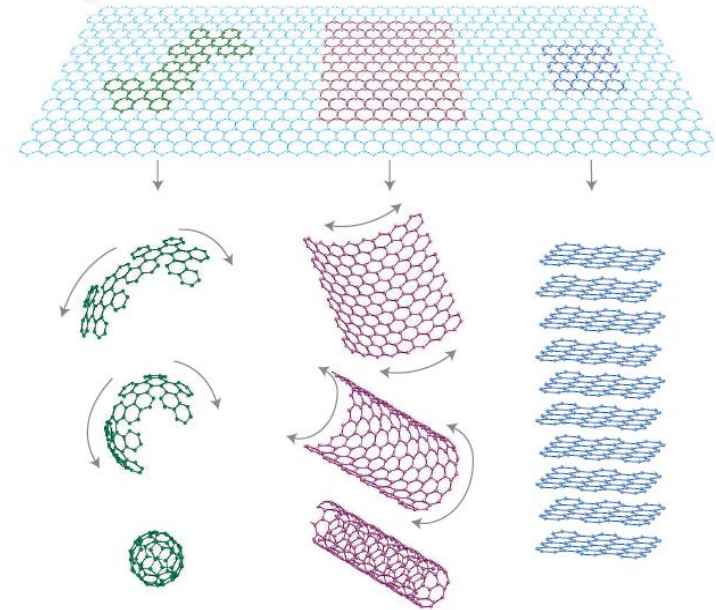


Molecular structure of graphene

Image source: <http://www.gizmag.com/polymer-graphene-substitute-kisi/32824/pictures>



High resolution transmission electron microscope (TEM) of graphene



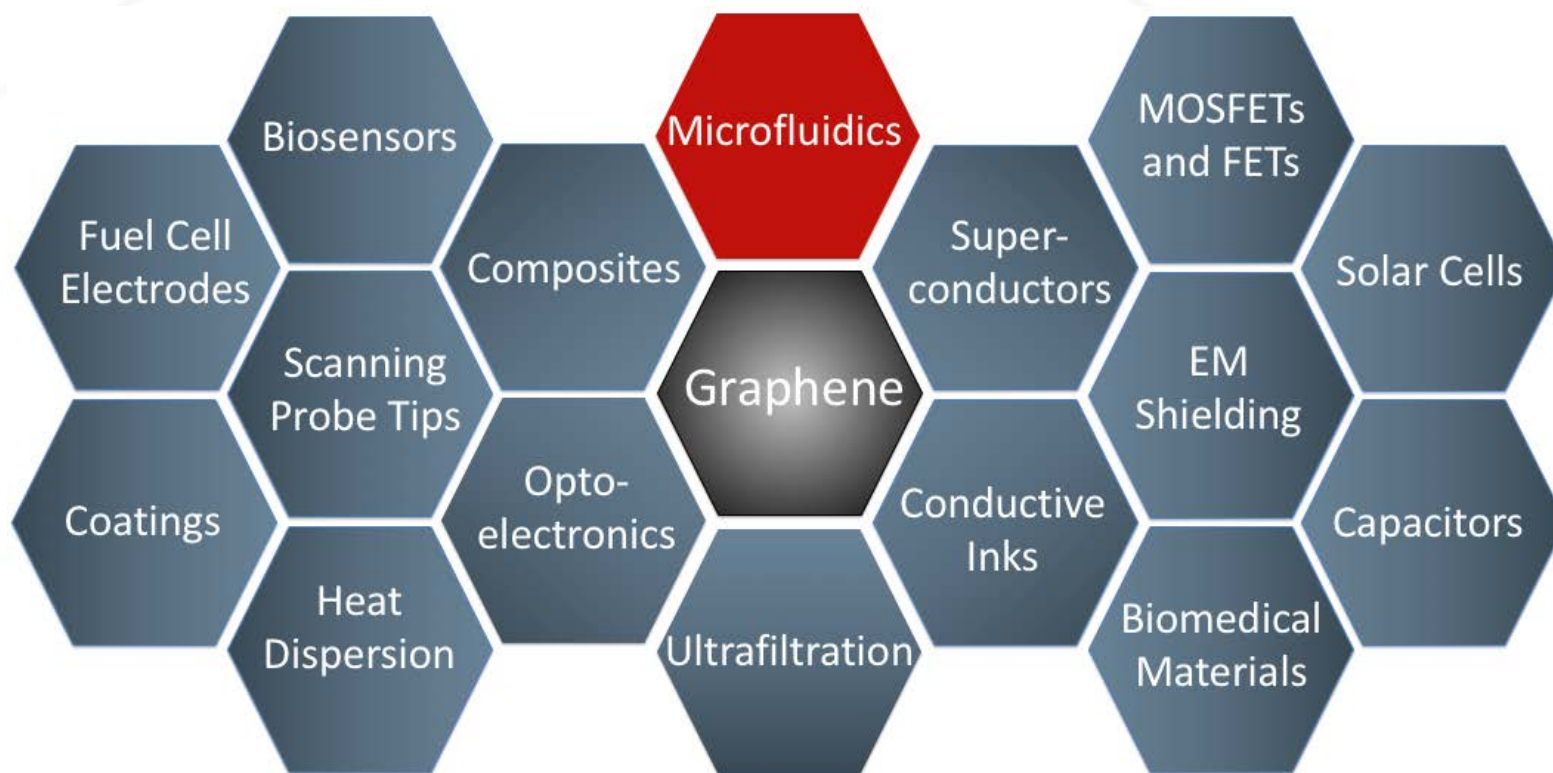
2D building material for carbon materials of all other dimensionalities

A. K. Geim & K. S. Novoselov, *Nature Materials*, 6, 183 -191, 2007.

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Graphene Applications



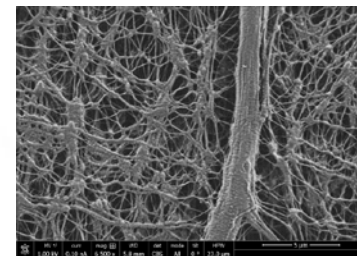
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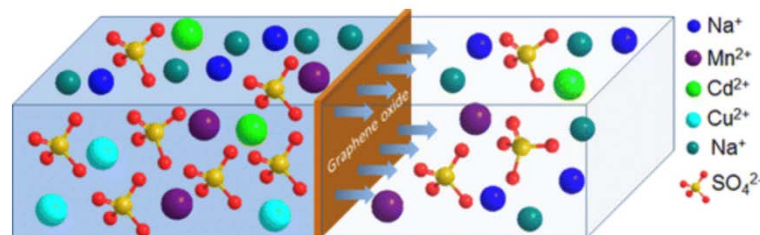
Why Graphene-based Membranes: Advantages

Advantages

- Ultra-thin, flexible, and chemically stable multi-functional graphene membranes with tunable and selective pores
- Current membranes are bulky and lead to a slow transfer rate in a microfluidic system.
- Large scale synthesis and functionalization of graphene is inexpensive and well established.
- Graphene can be modified by addition of metal nanoparticles and various functional groups.



SEM image of the current commercially available Teflon membranes with a thickness of 7.62 μm



P. Sun et al., "Selective Ion Penetration of Graphene Oxide Membranes", *ACS Nano*, 2013, 7 (1), pp 428–437.

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Why Graphene-based Membranes: Challenge

Free-standing graphene cannot be suspended over 100 μm wide channels without a supportive structure.

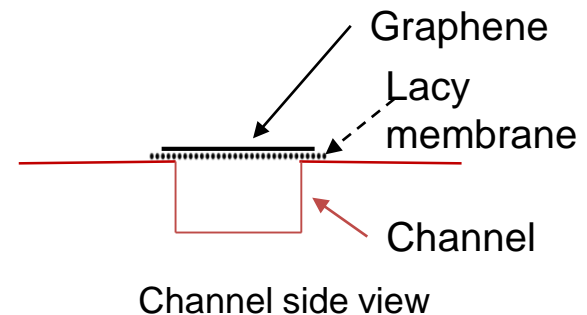
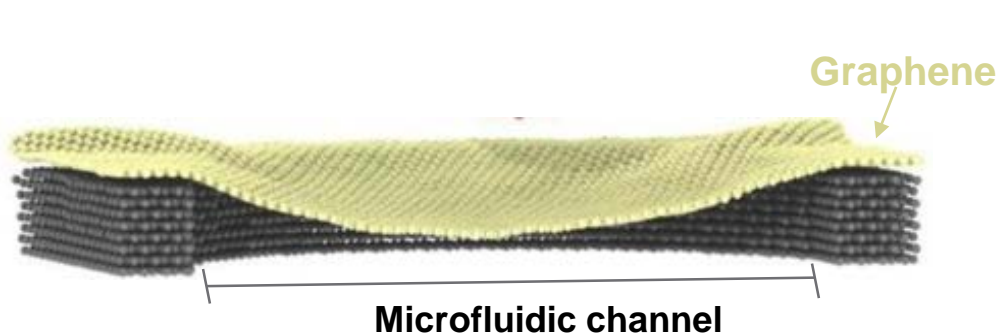
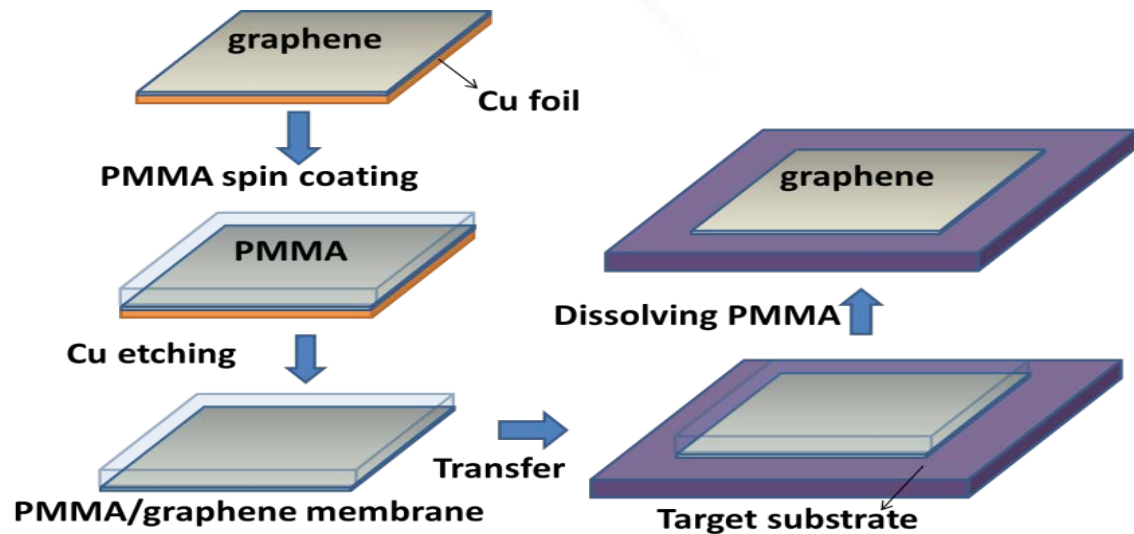


Image source: Lee et al. "Effect of Substrate Support on Dynamic Graphene/Metal Electrical Contacts." Micromachines 2018, 9, 169; doi:10.3390/mi9040169.

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Graphene transfer over the target substrate

- Graphene is synthesized by chemical vapor deposition on Cu.
- A polymer coating is first deposited over graphene and the Cu foil is removed.
- The polymer/graphene is placed over the target substrate before dissolving the polymer.

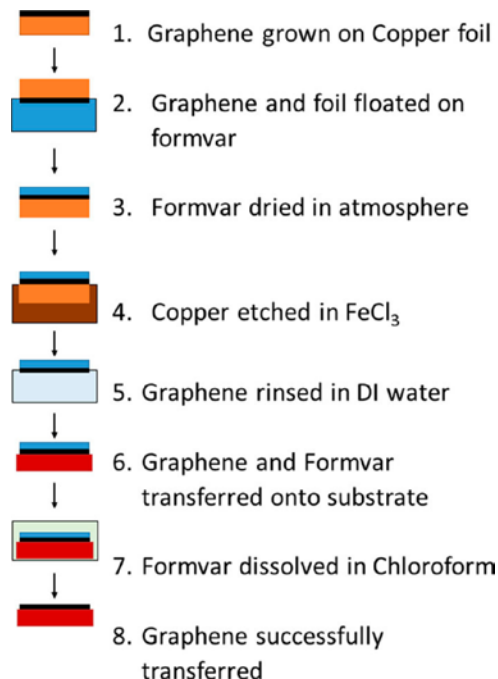


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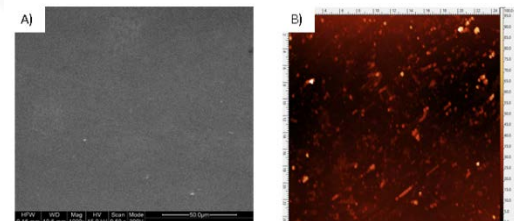
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Large-area graphene transfer via sacrificial polymer

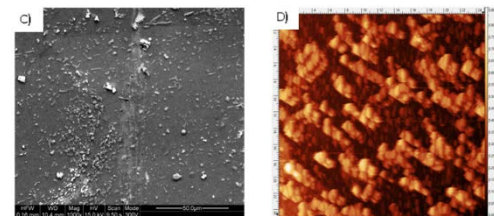
- A novel method of transferring large-area graphene sheets onto a variety of substrates using formvar (polyvinyl formal).
- This method allows for a rapid transfer of large sheets of graphene with less residue compared to the PMMA technique.



Formvar 1 minute



PMMA 1 minute



(A-B) SEM and AFM image of formvar/graphene/silicon after 1 min. in chloroform solution
(C-D) SEM and AFM image of PMMA/graphene/silicon after 1 min. exposure to acetone

E. Auchter, J. Marquez, S. L. Yarbrow, and E. Dervishi, "A facile alternate technique for large area graphene transfer via sacrificial polymer", AIP Advances, 7 (12), 125306, 2017.



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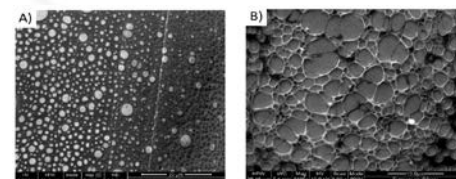
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Ultra-thin and strong formvar-based membranes with controlled porosity for micro- and nano-scale systems

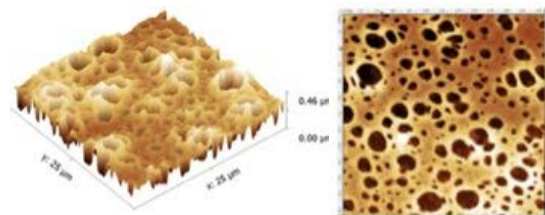
Graphene is supported over the channel via a lacey formvar membrane:

- Formvar is hydrophilic and oleophilic, inert to most chemicals, and resistant to radiation.
- Formvar is dissolved into solution and sonicated to form micrometer scale bubbles (tunable porosity 20% to 60%).
- Ultra-thin sheets have average thickness of **125 nm**.
- Model simulations indicate membrane porosity of 50% is optimal.

Manuscript Published: Dervishi et al., Nanotechnology, 29 (21), 215712, 2018.

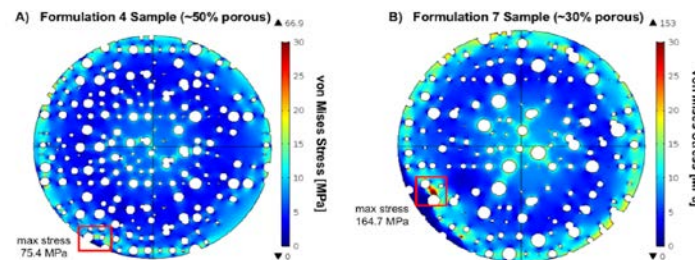


SEM images of holey vs. lacey formvar



AFM 3D surface render

Heatmap AFM

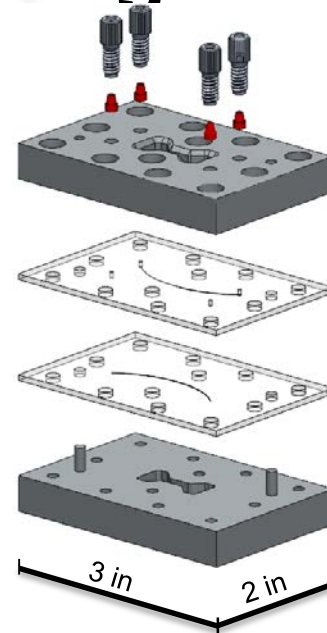


Model predictions of 125 nm thick formvar membrane under 400 Pa loading

Microfluidic System – Initial Design

Four part leak-free system to maintain phase separation in counter current flow while allowing for high rates of mass transfer:

- Two quartz chips with laser etched channels (100 μm wide and 100 μm deep)
- Membrane with a total thickness of ~ 250 nm is composed of graphene and formvar layers



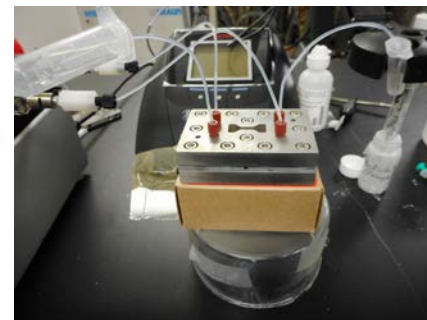
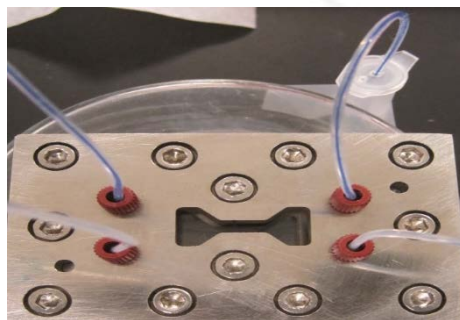
Inexpensive, small foot print and efficient system

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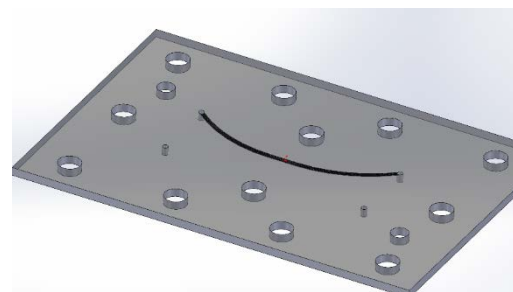
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Testing Parameters

- Chemical system consists of Water/n-Decane/Triethylamine.
- The ternary phase system is used to observe a pH change via ion transport from the organic phase to the aqueous phase.
- A pH change from ~neutral to upwards of 12 is observed.



Flow tests with xylenes and water demonstrating leak-free system



Quartz chips with 4 laser etched channels

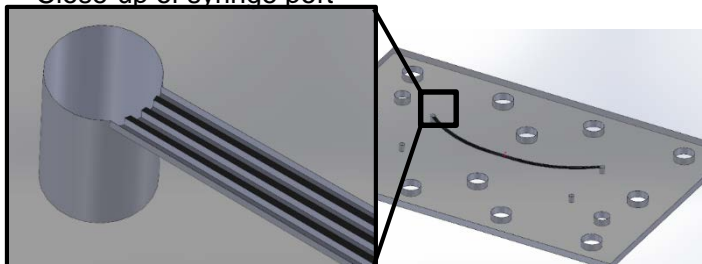
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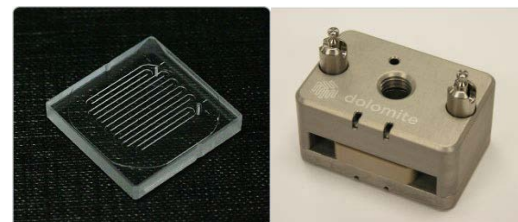
Microfluidic System - Designs

Device name	No. of channels	Flow type	Path length (mm)	Max Flow Rates ($\mu\text{L}/\text{min}$)
Single-Channel	1	Co-current	2.5	25
Single-Channel	1	Counter-current	2.5	25
Dolomite with Teflon membrane	1	Counter-current	500	1000
Four-Channel	4	Counter-current	5	100

Close-up of syringe port



Quartz chips with 4 laser etched channels

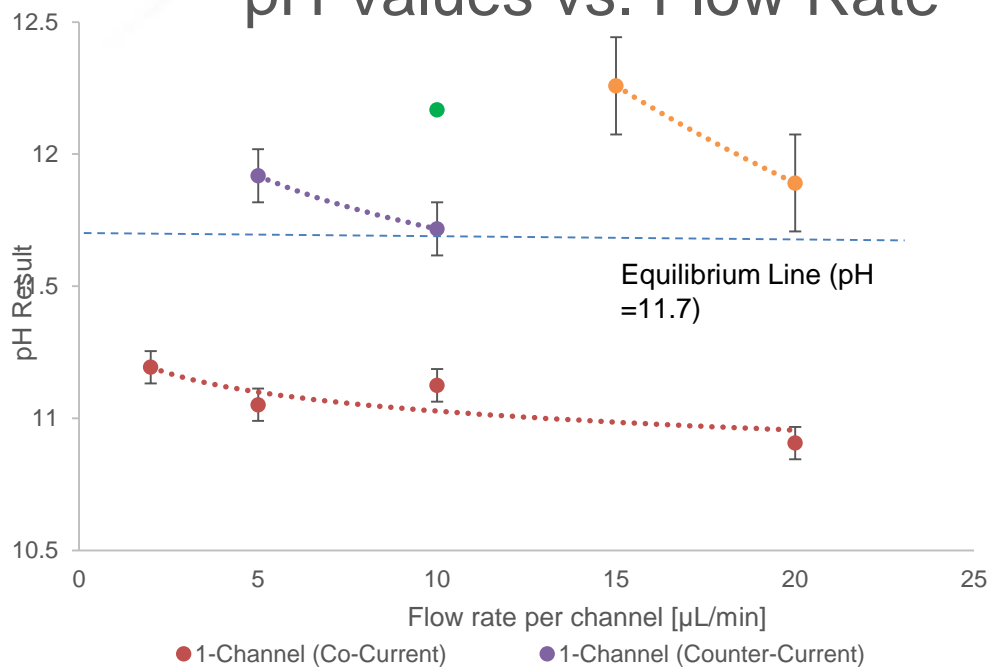


Membrane contactor: dolomite.com

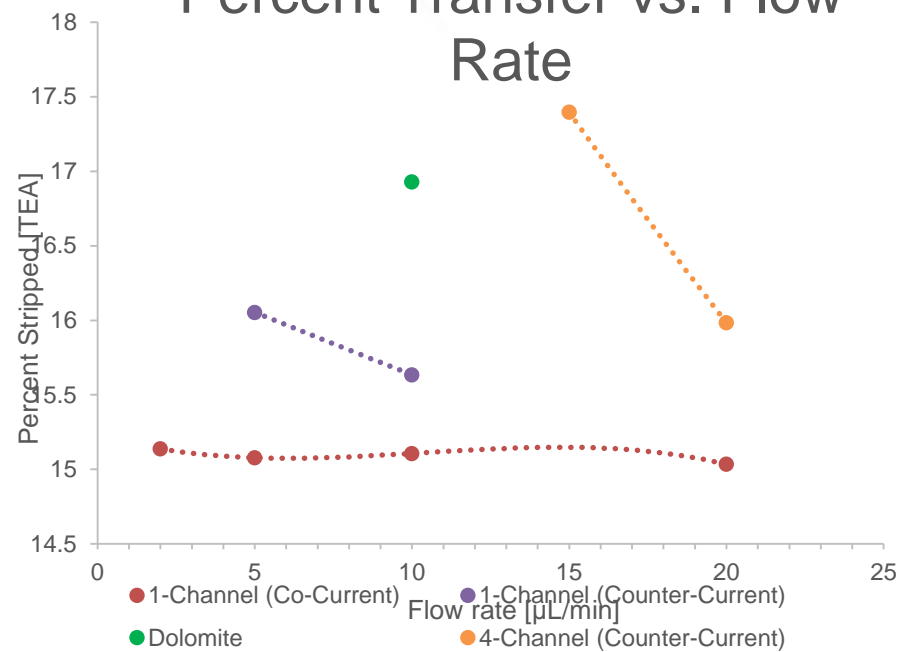
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Current Results

pH Values vs. Flow Rate



Percent Transfer vs. Flow Rate

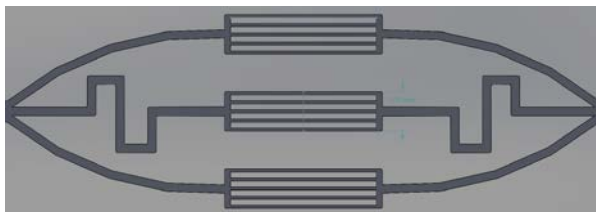


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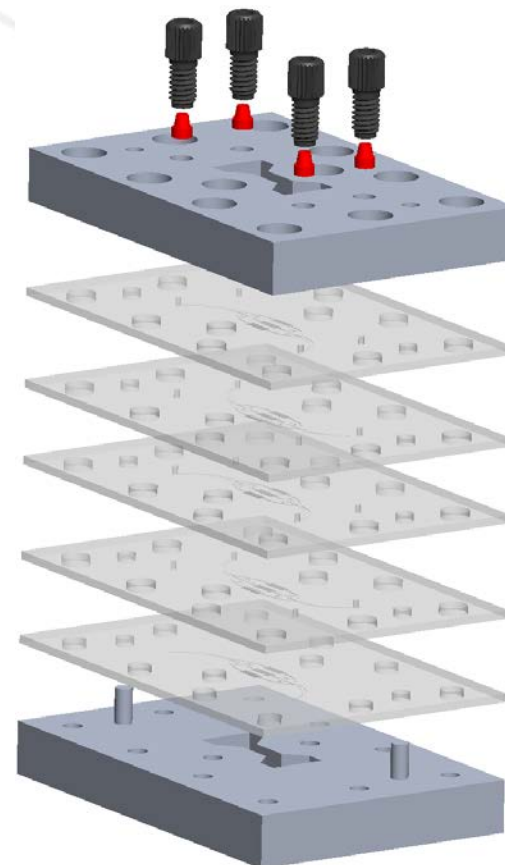
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Scalability

- Layering chips to achieve a 1.5 mL/min throughput
- Duplicating unit cells can make a chip with 75 channels per side with base design
- Base design is currently 3" x 2" x 1" and can be expanded in three dimensions



Unit cell of 15 parallel channels



Stacked Design with Unit Cell

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Scaling estimate

	Single chip (rectangular)	Multi chip (rectangular)	Circular Scaled device (cylindrical)
Size (inches)	3 x 2 x 1	3 x 2 x 2	6 \varnothing x 4 h
Number of channels per chip	4	75	1040
Fluid contact length (m)	0.005	0.48	10
Diffusion length (microns)	100	100	100
Flow rate (mL/min)	0.01	1.875	26
Number of quartz chips	1	25	<85 total layers
Cost: material + fabrication	~\$700	~\$2,800	<\$25,000



Holiday cookie tin,
roughly 6 \varnothing x 4 h

Image source: <https://m.macys.com/shop/product/original-gourmet-winter-wonderland-chocolate-chip-jumbo-holiday-cookie-tin?ID=2261494>

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Future Work

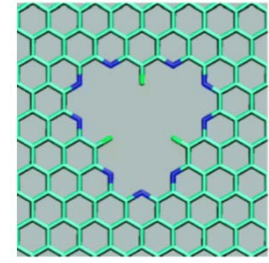
- Microfluidic Cell Assembled and Scalability Tests
>1ml/min flow rate:
 - Channel length
 - Parallel Channels
 - Multistage
 - Combination of parallel and series channel design
- Lithography Setup for new microfluidic testing
- New Actinide Chemistry
- Develop multifunctional graphene membranes by functionalization and doping

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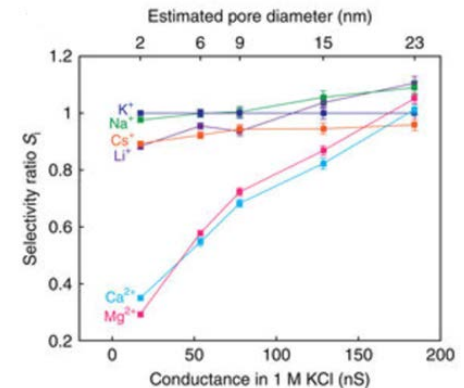
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Benefits of technology

- No moving parts
- Small size assembly
- Inexpensive low resolution photolithography fabrication
- Functionalized ultra-thin membranes with tunable porosities
- Microscale diffusion lengths
- Scalable in three dimensions to achieve large flow rates and path lengths
- Minimal pumping requirements
- Parallel and series countercurrent (flow) demonstrated



K. Sint et al., "Selective Ion Passage through Functionalized Graphene Nanopores" *J. Am. Chem. Soc.*, 2008, 130 (49),16448.

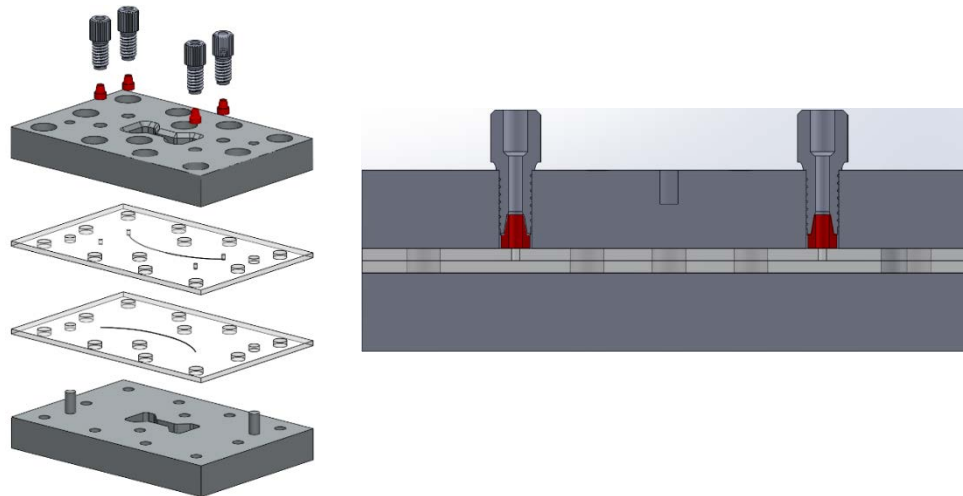


R. Rollings et al., "Ion selectivity of graphene nanopores", *Nature Communications*, 7, 11408 (2016) doi:10.1038/ncomms11408

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Invention Disclosure: Graphene Membrane Microfluidic System (Liquid-Liquid Extraction)

- Currently under review with the Laboratory Invention Disclosure Review Board (IDRB)

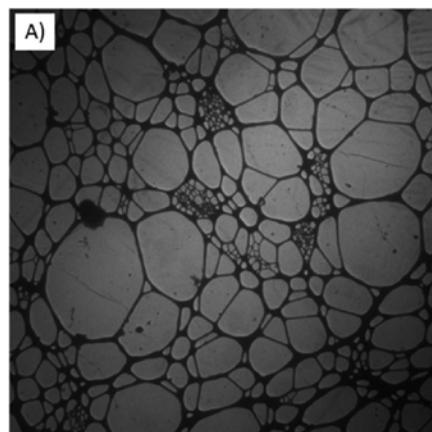


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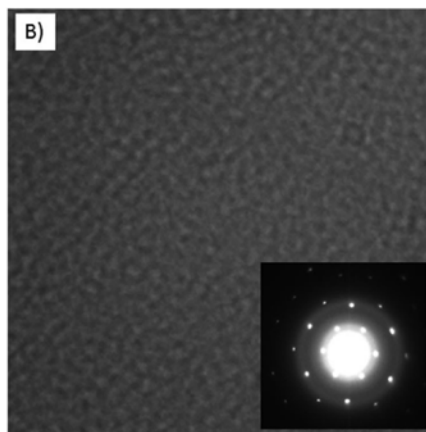
Invention Disclosure: Formvar Transfer of 2D Nanomaterials

- Submitted to IDRB on 1/11/2018



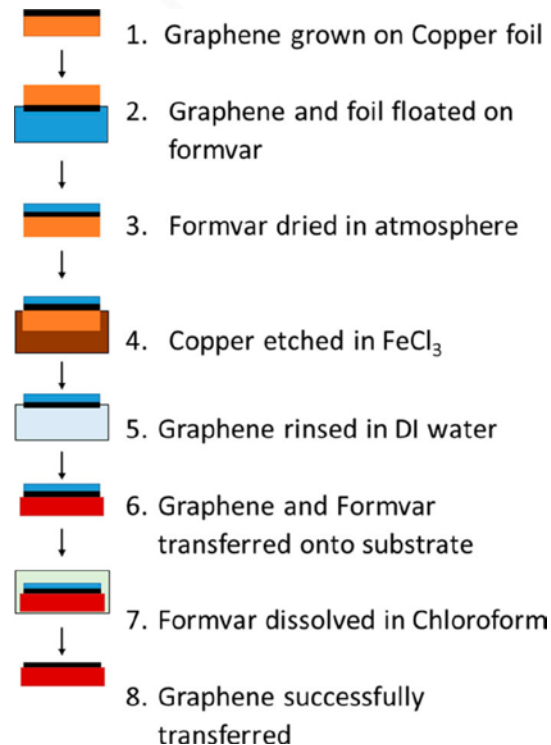
2 μm

FOV 20200 nm



100 nm

FOV 1500 nm



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Graphene Publications/Presentations

Papers:

- Auchter E. , Marquez J. , Yarbrow S. , and Dervishi E. , “A facile alternate technique for large area graphene transfer via sacrificial polymer”, AIP Advances, 7 (12), 125306, 2017.
- E. Auchter, J. Marquez, G. N. Stevens, R. Silva, Q. McCoulluch, Q. Guengerich, A. Blair, S. Litchfield, N. Li, C. Sheehan, R. Chamberlin, S. L. Yarbrow, and E. Dervishi, “Ultra-thin and strong Formvar-Based Membranes with Controlled Porosity for micro- and nano-scale systems”, Nanotechnology, 29 (21), 215712, 2018.
- Auchter E., Stevens G., Marquez J., Silva R., Li N., McCulloch Q., Guengerich Q., Litchfield S., Sheehan C., Chamberlin R., Yarbrow S.L., Dervishi E. “Development of graphene-based membranes for microfluidic systems”, Under preparation, 2018.

Posters/Presentations:

- Marquez J., Auchter E., Dervishi E. (2017). Porous Formvar membrane production and novel graphene transfer techniques. Presented at CINT User meeting in Santa Fe, NM.
- Marquez J., Auchter E., Dervishi E. (2017). High quality graphene and applications. Presented at LANL Student Symposium.
- Auchter E., Marquez J., Dervishi E. (2017). Development of Graphene and Formvar Membranes for Microfluidics. Poster presented at LANL 2017 Student Symposium and 2017 CINT User Meeting in Santa Fe, NM.
- Auchter E., Silva R., Dervishi E. (2016). Synthesis and Characterization of Large Area Graphene for use in Microfluidic Systems. Poster presented at CINT User Meeting in Santa Fe, NM.

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Acknowledgments

- *Post-Bac Students:* Andrew Blair, Justin Marquez, Eric Auchter, Trevor Wacht, Quintessa Guengerich, Sebastian Litchfield, Alison Hayley
- Garrison Stevens
- Janelle Droessler, Eric Meierdierk, George Goff
- Steve Yarbrow and Rebecca Chamberlin

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Thank you!

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